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Toxicity of Metalloid-Arsenic and its Remediation Mechanism(s)

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ABSTRACT

Arsenic (As) which is one of the highly toxic metalloids distributed ubiquitously in two inorganic forms viz. arsenite (AsIII) and arsenate (AsV), where, arsenite being more toxic form. Contamination level has spread to soil, sediments and other natural sources. Arsenic-mediated oxidative stress causes an array of metabolic dysfunctions in plant. Recently, globally, over 130 million people are potentially exposed to As in drinking water at levels above 10 µg/L. as per World Health Organization (WHO) guideline. Bioremediation depend on the fact that biological organisms have the ability to degrade, detoxify, and even accumulate harmful chemicals and offers attractive perspectives for biomonitoring, recycling and treatment of metal. Hence, strengthening awareness via public education is an urgent necessity for a sustainable As mitigation whole over the world.

Keywords: Arsenic, Distribution, Toxicity, Phytoremediation

1. INTRODUCTION:

The word Arsenic is a heavy metal derived from the Greek word arsenikon, which means potent. Arsenic (As) is found in nature in the earth's outer layer as the 20th most abundant element. Arsenic can enter environment from soil by wind or dust [1]. The primary supply of As is natural, derived primarily from the interactions between groundwater and geological formation sediments and hard rocks of minerals, particularly pyrite (FeS₂), arsenopyrite (FeAsS), and some of sulfide minerals which are unspecified [2, 3], the anthropogenic source of arsenic in ground water include agricultural activities, combustion and

mining of metal ore [4, 5]. As a results of such naturally occurring As and human-induced As concentrations, several groundwater systems greatly exceed the safe As guideline value of 10 µg/L counseled by the world Health Organization (WHO) [6-8]. Thus, the elevated As concentration in groundwater throughout the planet has received a lot of attention recently as a significant threat to public health similarly as for agricultural activities [9-11]. Arsenic uptake, metabolism, modulation and toxicity responses on crop plants have been discussed briefly in this review. An overview of inorganic Arsenic with an emphasis on: (1)

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natural processes, (2) Distribution, (3) transport mechanisms, and 4) Remediation. The main goal of this review is to provide a concise description of important naturally occurring geochemical processes that involve in the mobilization and distribution of Arsenic over global groundwater systems.

2. SOURCES OF ARSENIC:

Estimation of the presence time for arsenic in soil is 9000 years. Since arsenic is expected to remain in soil for centuries or longer, contaminated soil left at the site must be considered a potential source of exposure throughout this time frame [12]. Arsenic is released into the atmosphere in both inorganic and organic forms. Arsenate [As(V)] and arsenite [As(III)] are the inorganic, phytoavailable forms of arsenic in soil solution [13, 14].

Studies suggest that 70% of the total arsenic production in world is used in treatment of wood prepared for use in building and carpentry as copper chrome arsenate (CCA), 22% in farming chemicals, and the remaining in glass, pharmaceuticals and non-ferrous alloys production [15].

The industrial processes majorly are mining, smelting of non-ferrous metals and flaming of fossil fuels that contribute to anthropogenic arsenic contamination of air, water and soil. For the many years, use of arsenic-containing pesticides has left large tracts of agricultural ground polluted. In the maintenance of timber the use of arsenic has also led to contamination of the environment [16]. Arsenic is utilized industrially in the processing of glass, as an alloying agent, as well as pigments, textiles, paper, metal adhesives, wood preservatives and ammunition. Arsenic is also used in the hide

tanning process and, to a limited extent, in pesticides, feed added substances and drugs [17].

Tobacco smoking people can also be exposed to the natural inorganic arsenic content of tobacco because tobacco plants can take up arsenic naturally present in the soil. Also, in the past, the potential for elevated arsenic exposure was much higher when tobacco plants used to be treated with lead arsenate insecticide [18].

Rise of arsenic levels in soils causes significant concern with respect to plant uptake and subsequently enters into nature and human food chains.

3. DISTRIBUTION AND FACTORS AFFECTING DISTRIBUTION OF ARSENIC:

Arsenic normally occurs in nature: in air, soil, water, rocks, plants, and animals. Natural activities such as weathering, volcanic eruption, rock erosion, and forest fires may release As into the atmosphere [1]. Weathering is the key naturally happening process through which arsenic sulfides present in ores are transformed into a highly mobile form of As [As(V)], which may enter the As cycle directly as a dust or via dissolution in rainwater, water reservoirs, or groundwater [19]. As(III) also may travel widely among plants and animals through the food cycle. This prevalent distribution of As throughout the earth's crust, soil, sediments, water, air, and living organisms leads to serious unfavorable effects on the atmosphere. The occurrence of As in certain mineral phases, soil, and water systems is linked directly to the wide variety of As(III) and As(V) species in groundwater [20].

The original source of groundwater As in the Ganges–Meghna–Brahmaputra basin (India

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and Bangladesh) may have been the formation of the Himalayan orogenic belt by deep-seated tectono-magmatism resulting in the introduction of As to the surficial system by unearthing, after which it was transported by sedimentary processes to the peripheral foreland basin, where solid-phase As is released to the circulating groundwater by biogeochemical processes [1]. The intake of contaminated As (directly and/or indirectly through the food chain; i.e., arsenite and arsenate) was reported to induce carcinogenesis and cardiovascular disorders in Bangladesh and West Bengal, India [21].

Natural geochemical processes play a very important role in the release, transport, and distribution of As in groundwater. The conversion of As from the solid and/or semisolid phases to the aqueous phase is managed by several geochemical processes, including interfacial reactions such as adsorption/desorption, ion exchange, dissolution, and oxidation/reduction [1, 22]. The most general cause of As-rich groundwater is the release of As from iron oxide present in aquifer sediments. Iron oxide linked with felsic volcanic rocks and alkaline aquifers has been identified as a key source of As being released into the alkaline groundwater of the western USA [23].

The most dangerous threat to public health from arsenic originates from polluted groundwater. Argentina, Bangladesh, Chile, China, India, Mexico, and the United States of America countries reported for groundwater contamination by arsenic [24].

3.1 ARSENIC IN SOIL:

By the help of understanding the mechanisms of As uptake, accumulation and International Journal of Life Sciences and Technology (2022), Volume 14, Issue 1, Page(s):1-12

assimilation in crop plants The damaging effects of As on plants can be understood. Mostly of the As absorbed gets accumulated in the roots, and to a limited amount, in the aboveground parts of the plant [25, 26].

The As present in soil poses potential risk in surface and ground water [4]. In soil As is found in both organic and inorganic form, however inorganic As is the predominant form. Methylation of arsenic compounds by microorganisms produces monomethylarsonic acid, dimethylarsinic acid, and trimethylarsine oxide [1, 27]. Level of As depends upon climate, parent rock, organic and inorganic components of the soil, and redox potential status [28, 29]. Arsenate [As(V)] is the most stable form of As in soil and it can strongly be absorbed into clays, iron and manganese oxides/hydroxides, and organic matters found in soil in oxidizing conditions. In reducing conditions As(III) is dominant form of As. In many countries the Permissible levels of As in soil ranges from 0.1 to 40 mg/kg. The absorption of As in soil is depend upon bioavailability, mobility and presence of inorganic PO_4^{3-} , Ca^{2+} , and Na^+ in different types of soil, including Oxisol, Vertisol, and Alfisol, has a significant impact on the sorption of As(III) and As(V) [1].

4. EFFECT OF ARSENIC:

4.1 EFFECT ON PLANTS

The presence of As above the limit value in the soil or in the irrigation water alters the metabolism of the cultivated plants and leads to wilting, curling, necrosis of the leaf blade, suppression of the number of leaves and foliar area, which which reduces photosynthesis and biomass accumulation, loss of mineral content, reduction of elongation, proliferation and nodulation of

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roots, growth retardation and low yield [24, 30].

As-induced decrease in expressions of *nork*, *Enod2*, *N6* and *NIN* genes, while there was no change in the expression of *Enod40* and *ccs52* genes, resulting in fewer nodules and root proliferation in *Medicago sativa* L. During the Transcriptomic studies of *Medicago truncatula*, researchers developed a split-root system, where one part of the root system was exposed to the AsIII while the other was inoculated with *Ensifer medicae* bacteria. Their results revealed strong growth inhibition in AsIII exposed roots but not in the non-exposed roots, indicating a localised effect of As on root growth [31].

4.2 PHOTOSYNTHESIS:

Arsenic is broadly reported to reduce the rate of photosynthesis. Principally, As interferes with the synthesis of chlorophyll either through induction of Fe deficiency or by suppressing biosynthetic enzymes involved with chlorophyll synthesis [24, 32].

4.3 ARSENIC INDUCED CHANGES IN BIOCHEMICAL AND MOLECULAR LEVEL:

Arsenic exposure exerts harmful effects on carbohydrate metabolism of crop plants. Researchers observed in a steady decrease in the ratio of reducing/ non-reducing sugars in the shoot tissues of As-stressed *Oryza sativa* L [33, 34].

Presence of As in oxidation state in cells of plants results cellular injury. As III state is 100 times more toxic than the AsV, and this high toxicity is due to its affinity towards -SH groups of proteins [14]. AsIII combines with thiol-containing proteins and make them nonfunctional [35].

Exposure of arsenic has widely reported to induce genotoxic responses via excessive

production of ROS, in both plants and animals [36]. Plants are covered towards the ROS-induced damage with the aid of using an array of scavenging device that consists of enzymatic (SOD, CAT, POX, APX and GR) as well as non-enzymatic (GSH, carotenoids and ascorbate) compounds [37, 38]

Cellular membranes are sensitive sites of damages and the extent of membrane damage has been reported Under As stress conditions as a measure of stress tolerance capacity. Due to As stress imbalanced nutrient and water uptake inside plant cells, Cellular membranes get damaged which leads to reduced stomatal conductance [14].

4.4 EFFECT OF ARSENIC ON HUMAN HEALTH:

Risk of human exposure of As has greatly increased mainly due to the expansion of residential areas into former agricultural land. This results very adverse effect on human and environmental health [39]. Chronic exposure to As reasons many medical manifestations of which cutaneous lesions are the mostly reported [40, 41]. Melanosis (hyperpigmentation), keratosis, and leukomelanosis (hypopigmentation) are some of the arsenic-related clinical symptoms [42]. Arsenic is also known for carcinogen, causing skin, lung, bladder, liver, kidney cancers and other superficial cuticular diseases [43, 44]. Other health manifestations of arsenic toxicity include ischemic heart disease [45], and impaired cognitive abilities and motor functions [46]. The retinoic acid, thyroid hormone, oestrogen receptors and hormonal balance are also reported, affected by arsenic toxicity [47, 48].

4.5 EFFECT OF ARSENIC ON ANIMALS:

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Food and water contaminated with arsenic are channels via which this metalloids enters a animal body. There are some examples where derivatives of arsonic acid are fed to domestic animals to to enhance body growth and inhibit any future disease [13]. Arsenic poisoning is implicated by high mortality in the course of 2–3 days in homeothermal animals [49, 50]. Symptoms of arsenic poisoning are abdominal pain, weakness, salivation, nausea, necrosis of mucosal epithelia and degeneration of the renal tube and gastrointestinal capillaries and death in the ultimate scenario. Other effects include cutaneous arsenic exposure leads to drying up and deadening of the skin [51, 52]. In rodents Arsenic inhalation led to nasal flow discharge and eye irritation [50, 53]. Depression, dehydration, anorexia, frequent urination, and imbalance in body temperature are seen on prolonged exposure to arsenic contamination [49, 54, 55]. Post mortem examination of such affected individuals shows a reddened edematous gastric and intestinal mucosa, yellowing of the liver, and edema in the lungs. Symptoms of PNS abnormalities, anemia, leukopenia, melanosis, cardiac malfunction and liver damage was shown by lab animals. Surprisingly these symptoms were lost when exposure got refrained [51, 55, 56].

5. DETOXIFICATION OF ARSENIC TOXICITY:

The remediation or detoxification of arsenic form environment can be done by chemical or physical methods and bioremediation techniques also available which are eco friendly too.

5.1 CHEMICAL OR PHYSICAL METHODS:

5.1.1 Coagulation–precipitation. In the process of Coagulation–precipitation

chemicals transform dissolved arsenic into an insoluble solid which is precipitated. Arsenic that has been dissolved in water may be adsorbed on the surface and precipitated with other precipitating species. Coagulation and flocculation can also be used to separate suspended/colloidal arsenic. The removal efficiency is heavily influenced by the pH of the procedure. Generally used chemicals in this technique are ferric salts, alum, manganese sulphate, ammonium sulphate, copper sulphate, etc [57-59].

5.1.2. Lime softening. Limes (lime stone, calcium hydroxide) are applied for the removal, similarly to precipitation [57].

5.1.3. Adsorption. Arsenic species are physically and chemically bound to the surface of the adsorbent in this approach. The removal efficiency is heavily influenced by the active surface area of the adsorbent, its surface energy, and the pH of the solution. Activated alumina, activated carbon, greensand (KMnO₄ coated gluconite), granular ferric hydroxide, iron oxide coated sand, copper-zinc granules, and other adsorbents are commonly used [57, 58, 60].

5.1.4. Ion exchange. In this approach arsenic ions electro statically retained on the surface of a strong base anion exchange resin are exchanged for ions of equal charge in the solution from the resin [57, 61].

5.1.5. Membrane filtration. Arsenic is removed from water using this approach, which involves passing it through a semi permeable barrier or membrane. The separation is propelled by a pressure difference. The removal effectiveness is determined by the membrane pore size and the particle size of the arsenic species. The

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removal efficiency can be enhanced by a pre-oxidation process [57, 62].

5.1.6. Electro dialysis. The driving force for separation is generated by an electric field applied across a semi permeable membrane in the polluted water, similar to reverse osmosis [57, 63].

5.2 Bioremediation methods / Phytoremediation methods

Bioremediation is a field of biotechnology that involves removing contaminants, pollutants, and toxins from soil, water, and other environments using living organisms such as microorganisms and bacteria. Oil spills or polluted groundwater are cleaned up by bioremediation [64].

Phytoremediation is a bioremediation method that uses various types of plants to eliminate, transfer, stabilize, and/or destroy contaminants in the soil and groundwater. There are some different types of phytoremediation mechanisms [65]. These are:

5.2.1 Rhizosphere biodegradation. In the process of Rhizosphere biodegradation, plants release natural substances through the roots to supply nutrients to microorganisms present in the soil which enhances the biological degradation [66].

Phenolics releasers (mulberry, apple, orange); Grasses with fibrous roots (rye, fescue, Bermuda) for contaminants 0-3 ft deep; Phreatophyte trees for 0- 10 ft; Aquatic plants for sediments are used in this process [67].

Das et al. found hyperaccumulator plant *Pteris vittata* have a role in mitigation of As toxicity and to promote growth and the As uptake ability of *P. vittata* under As-enriched conditions [68].

5.2.2 Phytostabilization. Phytostabilization is defined as (1) immobilization of contaminant in soil through absorption and accumulation by roots, adsorption onto roots, or precipitation within the root zone of plants, and (2) the use of plants and plant roots to prevent contaminant migration via wind and water erosion, leaching, and soil dispersion. Phytostabilization occurs through root-zone microbiology and chemistry, and/or alteration of the soil environment or contaminant chemistry. Soil pH may be changed by plant root exudates or through the production of CO₂ [26]. Wu et al. suggested that *A. corniculatum* is a potential candidate mangrove species for As phyto-stabilization in tropical and subtropical estuarine wetlands [69] and also find Mangrove species *A. corniculatum* is an As excluder with an innate capacity to tolerate As stress. Phreatophyte trees to transpire large amounts of water for hydraulic control; Grasses with fibrous roots to stabilize soil erosion; Dense root systems are needed to sorb / bind contaminants [67]

5.2.2 Phyto-accumulation (also called phyto-extraction). In this method, plant roots sorb the contaminants beside different nutrients and water. The pollutant mass isn't destroyed however lands up within the plant shoots and leaves. This method is used mostly for phytoremediation of wastes containing metals.

High As accumulation and tolerance potential of *C. procera* from artificially As contaminated water and soil coupled with good growth and its phytoextraction ability suggests the feasibility of this plant

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for the phytoremediation of As from contaminated water and soils [70].

Some examples are given, plants which used in phyto-extraction Sunflowers, Indian mustard, Rape seed plants, Barley, Hops, Crucifers, Serpentine plants [67].

5.2.3 Hydroponic Systems for Treating Water

Streams (Rhizofiltration). Rhizofiltration is a form of phytoremediation that involves filtering contaminated groundwater, surface water and wastewater through a mass of roots to remove toxic substances or excess nutrients [71]. Typically hydroponic systems utilize an artificial soil medium, such as sand mixed with perlite or vermiculite. As the roots become saturated with contaminants, they are harvested and disposed of [72].

A few examples of plants that are used for rhizofiltration are sunflower, tobacco, spinach, rye and Indian mustard [73]

Eleocharis macrostachya is an arsenic-tolerant plant with the capability of rhizofiltrating arsenic from water, which has good removal efficiency of arsenic from water [74].

5.2.4 Phyto-volatilization. Naturally occurring or genetically modified plants that are capable of absorbing elemental forms of these metals from the soil, biologically converting them into gaseous species within the plant, and releasing them into the atmosphere. This process is called phyto-volatilization. Sakakibara et al. suggested that *P. vittata* effectively volatilizes As; it removed a maximum ratio of 90% of the total uptake of As from As-contaminated soils [75].

Other examples of plants use in phyto-volatilization are Poplar, Indian mustard, Canola, Tobacco [67].

5.2.5 Phyto-degradation. Phytodegradation which is specifically also called “phytotransformation, is the method in which plants degrade organic pollutants by metabolic processes using the rhizospheric associations between plants and soil microorganisms [26].

Phreatophyte trees (poplar, willow, cottonwood); Grasses (rye, Bermuda, sorghum, fescue); Legumes (clover, alfalfa, cowpeas) are some examples of plants use in phyto-deradation [67].

Li, Ling, et al. suggested that *Thysanolaena maxima* (TM) is suitable for phyto-extraction of As in contaminated soils [76].

Hydraulic Control. Hydraulic control is additionally referred to as phytohydraulics or hydraulic plume control. It is use of plants to remove groundwater through uptake and consumption so as to contain or control the migration of contaminants [26].

Phreatophytes, plants such as cottonwood (*Populus* spp.), willow (*Salix* spp.), and salt cedar (*Tamarix* spp.) are used in the hydraulic control phytoremediation [77]

6. CONCLUSION:

Arsenic can be introduced in the environment either by natural processes or by anthropogenic actions. The geochemistry of As is a complex phenomenon in the environment, and it is generally a function of multiple oxidation states, speciation, and redox transformation. The toxicity of various

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forms of As depends on chemical structure and their oxidative states. Arsenic basically interferes with metabolic processes, inhibits plant growth and development via phytotoxicity. Arsenic is also a well-known carcinogen in animals. Although several cytotoxic and genotoxic effects of As in crop plants have already been suggested, yet its molecular mechanisms remains obscure and it is unclear how As-toxicity can be minimized without inducing any permanent damage in the plants. Moreover, efforts should be made to unravel the exact molecular mechanisms behind amelioration of As-induced toxicity responses in crop plants using ROS quenchers like proline, NO, SA and polyphenols.

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